Inter (Part-I) 2016

Chemistry	Group-I	PAPER: I
Time: 2.40 Hours	(SUBJECTIVE TYPE)	Marks: 68

SECTION-I

2. Write short answers to any EIGHT (8) questions: (16)

(i) N_2 and CO has the same number of electrons, protons and neutrons. Justify it.

Ans **No. of electrons:**

$N_2 \longrightarrow N + N \longrightarrow 7e^- + 7e^- = 14$ electrons

$CO \longrightarrow C + O \longrightarrow 6e^- + 8e^- = 14$ electrons

No. of protons:

$N_2 \longrightarrow N + N \longrightarrow 7p + 7p = 14$ protons

$CO \longrightarrow C + O \longrightarrow 6p + 8p = 14$ protons

No. of neutrons:

$N_2 \longrightarrow N + N \longrightarrow 7n + 7n = 14$ neutrons

$CO \longrightarrow C + O \longrightarrow 6n + 8n = 14$ neutrons

So, N_2 and CO have the same number of electrons, protons and neutrons.

(ii) Calculate the number of moles of O atoms in 9.00 gram of $Mg(NO_3)_2$.

Ans **Data:**

Mass of $Mg(NO_3)_2$ = 9 g

Molar mass of $Mg(NO_3)_2$ = $24 + 2(14 + 3 \times 16)$ = 148 g mol^{-1}

$$\text{Number of moles} = \frac{\text{Mass given of } Mg(NO_3)_2}{\text{Molar mass of } Mg(NO_3)_2}$$

Putting the values

$$\text{Number of moles} = \frac{9 \text{ g}}{148 \text{ g mole}^{-1}} = 0.06$$

1 mole of $Mg(NO_3)_2$ contains moles of O atoms = 6

0.06 moles of $Mg(MO_3)_2$ contain moles of O atoms = 0.06×6

$= \boxed{0.36}$ Ans.

(iii) Define molecular ion. How it is formed?

Ans When an atom loses or gains an electron, it forms an ion. Similarly, a molecule may also lose or gain an electron to form a molecular ion, *e.g.*, CH_4^+, CO^+, N_2^+. Cationic molecular ions are more abundant than anionic ones. These ions can be generated by passing high energy electron beam as α-particles or X-rays through a gas. The break down of molecular ions obtained from the natural products can give important information about their structure.

(iv) How crystals are dried by reliable method?

Ans A safe and reliable method for drying crystals is through a vacuum desiccator. In this process, the crystals are spread over a watch glass and kept in a vacuum desiccator for several hours. The drying agents used in a desiccator are $CaCl_2$, silica gel or phosphorus pentaoxide. Crystals do not damage in this method. The shape of crystal remains constantly unchanged.

(v) Write four properties of a good solvent.

Ans An ideal solvent should have the following features:

1. It should dissolve a large amount of the substance at its boiling point and only a small amount at the room temperature.
2. It should not react chemically with the solute.
3. It should either not dissolve the impurities or the impurities should not crystallize from it along with the solute.
4. On cooling, it should deposit well-formed crystals of the pure compound.

(vi) Calculate the value of 'R' gas constant in SI units.

Ans **Value of R in SI unit:**

For calculating the value of R, we must consider the S.I units of pressure, volume, temperature.

S.I unit of pressure = Nm^{-2}

S.I unit of temperature = K

S.I unit of volume = m^3

1 atm = 760 torr = 101325 Nm^{-2}

1 m^3 = 1000 dm^3

$n = 1$ mole
$T = 273.16$ K
$P = 1$ atm $= 101325\ Nm^{-2}$
$V = 22.414\ dm^3 = 0.022414\ m^3$
Putting their values along with units.
From $PV = nRT$, we get:

$$R = \frac{PV}{nT}$$

$$R = \frac{101325\ Nm^{-2} \times 0.022414\ m^3}{1\ mol \times 273.16\ K}$$

$$R = 8.3143\ Nm\ K^{-1}\ mol^{-1}$$

$$= 8.3143\ J\ K^{-1}\ mol^{-1} \quad (1\ Nm = 1\ J)$$

Since, 1 cal. = 4.18 J

So, $$R = \frac{8.3143}{4.18}$$

$$= 1.989\ cal.\ k^{-1}\ mol^{-1}$$

(vii) State Avogadro's law of gases. Give two examples.

Ans **Definition:**

Equal volumes of all the gases at same temperature and pressure contain equal number of molecules.

Reason:

1 dm^3 of H_2 gas has a mass = 0.0899 g
1 dm^3 of O_2 gas has a mass = 1.4384 g

(viii) The plot of PV versus P is a straight line at constant temperature and with a fixed number of moles of an ideal gas. Justify.

Ans A straight line parallel to the pressure axis. This straight line indicates that 'k' is a constant quantity. At higher constant temperature, the volume increase and value of product PV should increase due to increase of volume at same pressure, but PV remains constant at this new temperature and a straight line parallel to the pressure axis is obtained. This type of straight line will help us to understand the non-ideal behaviour of gases. Boyle's law is applicable only to ideal gases.

(ix) Define solubility product. Derive solubility product expression for sparingly soluble compound Ag_2CrO_4.

Ans "The product of molar solubilities of the ions of a weak electrolyte at equilibrium stage is called solubility product."

It is denoted by K_{sp}. The K_{sp} of the salts are very small quantities and they are temperature dependent.

Ion Product	K_{sp}
$[Ag^{\oplus}]2[CrO_4]2$	2.6×10^{-12}

(x) Calculate the pH of 10^{-4} mole dm^{-3} of $Ba(OH)_2$.

Ans $Ba(OH)_2$ is also a strong electrolyte, and is dissociated 100% at very low concentrations of 10^{-4} mol. dm^{-3}.

$$Ba(OH)_2 \rightleftharpoons Ba^{2+} + 2OH^{\ominus}$$

$$10^{-4} \text{ moles dm}^{-3} \rightleftharpoons 0 + 0$$

$$0 \rightleftharpoons 10^{-4} + 2(10^{-4})\ t = \text{equilibrium}$$

So, $[OH^{\ominus}] = 2(10^{-4}) = 2 \times 10^{-4}$

Formula Applied:

$$POH = -\log[OH^{\ominus}]$$

Putting the values

$$POH = -\log 2 \times 10^{-4}$$

$$POH = 3.69$$

Since, $pH + pOH = 14$

Therefore, $pH = 14 - pOH = \boxed{10.31}$

(xi) Why aqueous solution of CH_3COONa is basic in nature?

Ans For CH_3COONa, the reaction with water is:

$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$$

The acetate ion is hydrolyzed in water to give CH_3COOH and OH becomes free. Na^+ is not hydrolysed. The result is that the solution becomes basic in nature.

(xii) What are the name of four major parts of apparatus used in Landsberger's method for elevation of boiling point?

Ans The apparatus consists of four major parts:

1. An inner tube with a hole in its side. This tube is graduated.

2. A boiling flask which sends the solvent vapours into the graduated tube through a rosehead.
3. An outer tube, which receives hot solvent vapours coming from the side hole of the inner tube.
4. A thermometer which can read up to 0.01K.

3. Write short answers to any EIGHT (8) questions: (16)

(i) Why does evaporation cause cooling?

Ans Evaporation causes cooling because when high energy molecules leave the liquid and low energy molecules are left behind, the temperature of liquid falls and heat moves from surrounding to liquid and then temperature of surrounding also falls.

(ii) Define molar heat of fusion and molar heat of vaporization.

Ans **Molar Heat of Fusion (ΔH_f):**

It is the amount of heat absorbed by one mole of a solid when it melts into liquid form at its melting point. The pressure, during the change is kept one atmosphere.

Molar Heat of Vapourization (ΔH_v)

It is the amount of heat absorbed when one mole of a liquid is changed into vapours at its boiling point. The pressure, during the change is kept one atmosphere.

(iii) What is transition temperature? Give its one example.

Ans It is that temperature at which two crystalline forms of the same substance can co-exist in equilibrium with each other. At this temperature, one crystalline form of a substance changes to another.

Example:

$$Na_2SO_4 - 10H_2O \text{ (hydrated form)} \xrightleftharpoons{32.38^\circ C} \underset{\text{(anhydrous form)}}{Na_2SO_4} + 10H_2O$$

(iv) Write four properties of molecular solids.

Ans Following are the four properties of molecular solids:

1. X-ray analysis has shown the regular arrangements of atoms in constituent molecules of these solids, and we get the exact positions of all the atoms.
2. The forces, which hold the molecules together in molecular crystals, are very weak, so they are soft and easily compressible.

3. They are mostly volatile and have low melting and boiling points. They are bad conductors of electricity, have low densities and sometimes transparent to light. Polar molecular crystals are mostly soluble in polar solvents, while non-polar molecular crystals are usually soluble in non-polar solvents.
4. Iodine is one of the best examples of a molecular solid. Let us discuss the structure of iodine molecule.

(v) Cathode rays are material in nature. Justify it.

Ans Cathode ray tubes use an interesting and varied assemblage of raw materials. In many cases, it is raw materials, not design or manufacturing process, that determining the performance characteristic of finished product.

(vi) Write the two drawbacks of Rutherford's model of atoms.

Ans Following are two defects of Rutherford's Atomic Model:

1. The outer electrons could not be stationary.
2. The behaviour of electrons remained unexplained in the atom.

(vii) Define Heisenberg's uncertainty principle and give its mathematical expression.

Ans Certainty in the determination of one quantity introduces uncertainty in the determination of the other quantity.

Suppose that Δx is the uncertainty in the measurement of the position and ΔP is the uncertainty in the measurement of momentum of an electron, then:

$$\Delta x \, \Delta p \geq \frac{h}{4\pi}$$

This relationship is called uncertainty principle.

(viii) What is orbital? Draw the shape of P orbital.

Ans

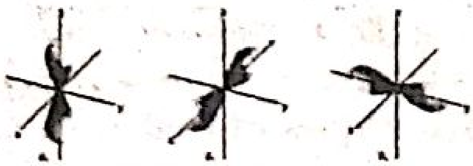

Fig. Shapes of p-orbitals.

Orbital:

According to idea of hybridization, atomic orbitals differing slightly in energy intermix to form new orbitals, which are called

hybrid atomic orbitals. They differ parent atomic orbitals in shape and possess specific geometry.

(ix) Differentiate between molarity and molality.

Ans **Molarity:**

It is the number of moles of solute dissolved per dm^3 of the solution.

$$M = \frac{\text{Mass of solute}}{\text{Mol. mass of solute}} \times \frac{1}{\text{Volume of solution in dm}^3}$$

Molality:

It is the number of moles of solute in 1000 g (1 kg) of the solvent.

$$M = \frac{\text{Mass of solute}}{\text{Mol. mass of solute}} \times \frac{1}{\text{Mass of solvent in kg}}$$

(x) Calculate the oxidation number of manganese in $KMnO_4$.

Ans

Oxidation no. of K $= +1$

Oxidation no. of O $= -2$

Oxidation no. of Mn $= x$

By putting values:

$$+1 + x + 4(-2) = 0$$
$$1 + x - 8 = 0$$
$$-7 + x = 0$$
$$x = 7$$

Oxidation no. of Mn = 7

(xi) What is function of salt bridge in voltaic cell?

Ans **Function of Salt Bridge:**

The purpose of the salt bridge is to prevent any net charge accumulation in either beaker by allowing negative ions to leave the right beaker, diffuse through the bridge and enter the left beaker. If this diffusional exchange of ions does not occur, the net charge accumulating in the beakers would immediately stop the flow of electrons through the external circuit and the oxidation-reduction reaction would stop.

(xii) Write two advantages of fuel cells.

Ans Here are two advantages of fuel cell:

1. The fuel cell is operated at a high temperature, therefore, water formed is evaporated.

2. A number of fuel cells are connected together to obtain several kilowatt power.

4. Write short answers to any SIX (6) questions: (12)

(i) Why the abnormality of bond length and bond strength in HI is less prominent than that of HCl?

Ans Chlorine has higher electronegativity than iodine. So, the polarities of HCl and HI bonds are unequal. Therefore, abnormality of bond length and bond strength of HCl is more prominent than HI.

(ii) Why the dipole moment of CO_2 is zero but that of SO_2 is 1.61 D?

Ans The dipole moments of CO_2 is zero because CO_2 have linear structure, where the dipoles being equal and opposite, cancel other's effect, whereas, dipole moment of SO_2 is 1.61 D because SO_2, a triatomic molecule, has an angular structure with bond angle 104.5°.

(iii) Why the melting points, boiling points, heat of sublimation and heat of vaporization of electrovalent compounds are higher as compared with those of covalent compounds?

Ans Electrovalent (ionic) compounds have high melting and boiling points due to close packing of oppositely charged ions. The positively charged ions are surrounded by negatively charged ions and vice versa. Therefore, ionic compounds have high melting points, boiling points, heat of vapourization and heat of sublimation than the covalent compounds.

(iv) Why BF_3 is non-polar but SO_2 is polar?

Ans **BF_3:**

Symmetry of trigonal planer shape means that three bonds moments exactly cancel one another. A molecule possess bonds and still non-polar or positive charge than another side and so, BF_3 is non-polar. In BF_3, boron has sp^2 hybridization.

SO_2:

SO_2 is not symmetrical, so there is region of unequal sharing. The oxygen at bottom of structure is more than negative. Therefore, SO_2 is polar.

(v) **Differentiate between law of conservation of energy and Hess's law.**

Ans **Hess's law:**

The enthalpy change of a system depends upon its initial and final states only. It is independent of path followed by system.

Law of Conservation of energy:

Law which states energy cannot be created or destroyed, but may be changed from one form to another.

(vi) **Why is it necessary to mention the physical states of reactants and products in a thermochemical equation of a reaction?**

Ans The substances exist because they possess energy. Whenever a substance changes its physical state or a phase change happens then it changes its energy. So in thermochemical reactions, it is necessary to mention the physical states of reactants and products.

Let us take an example of water synthesis from H_2 and O_2, when both of the reactants are in the gaseous state.

If liquid water is produced than 285.8 kJ mol^{-1} of energy is evolved. But when water is produced in the vapour state 241.5 kJ mol^{-1} of energy is evolved. Actually 44.3 kJ mol^{-1} of energy is used up to vapourize 1 mole of water at its boiling point. This is called heat of vapourization of water.

Hence, we will write the two reactions as follows:

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(g)} \quad \Delta H = -241.5 \text{ kJ mol}^{-1}$$

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)} \quad \Delta H = -285.8 \text{ kJ mol}^{-1}$$

(vii) **How surface area affects the rate of reaction? Give one example**

Ans The increased surface area of reactants, increases the possibilities of atoms and molecules of reactants to come in contact with each other and the rates enhance. For example, *Al* foil reacts with NaOH moderately when warmed, but powdered *Al* reacts rapidly with cold NaOH and H_2 is evolved with frothing.

$$2Al + 2NaOH + 6H_2O \longrightarrow 2NaAl(OH)_4 + 3H_2$$

(viii) What do you mean by activation energy of a reaction?

Ans The minimum amount of energy required for an effective collision is called activation energy.

(ix) What is autocatalyst? Give one example.

Ans "In some reactions, a product formed acts as a catalyst. This phenomenon is called as auto-catalysis."

Example:

When copper is allowed to react with nitric acid, the reaction is slow in the start. It gains the speed gradually and finally becomes very fast. This is due to the formation of nitrous acid during the reaction which accelerates the rate of reaction.

SECTION-II

NOTE: Attempt any Three (3) questions.

Q.5.(a) NH_3 gas can be prepared by heating together two solids NH_4Cl and $Ca(OH)_2$. If a mixture of 100 gm of each solid is heated then calculated the number of grams of NH_3 produced: **(4)**

$$2NH_4Cl_{(s)} + Ca(OH)_{2(s)} \rightarrow CaCl_{2(s)} + 2NH_{3(g)} + 2H_2O_{(l)}$$

Atomic mass of H = 1.008, N = 14, Cl = 35.5, O = 16, Ca = 40

Ans Following are the properties of cathode rays:

(1) Cathode rays are negatively charged.

(2) They produce a greenish fluorescence on striking the walls of the glass tube.

(3) Cathode rays cast a shadow when an opaque object is placed in their path.

(4) These rays can drive a small paddle wheel placed in their path.

(5) Cathode rays can produce X-rays when they strike an anode particularly with large atomic mass.

(6) Cathode rays can produce heat when they fall on matter.

(7) Cathode rays can ionize gases.

(8) They can cause a chemical change, because they have a reducing effect.

(9) Cathode rays can pass through a thin metal foil like aluminium or gold foil.

(10) The e/m value of cathode rays shows that they are simply electrons.

(b) Define liquid crystals and give their three uses. (4)

Ans There are many crystalline solids which melt to a turbid liquid phase before finally melting to a clear liquid. These turbid liquid phases can flow as liquids, have surface tension and viscosity. These turbid liquids are called as liquid crystals.

Uses of Liquid Crystals:

(i) Potential failure:

Liquid crystals are used to find the point of potential failure in electrical circuits. Room thermometers also contain liquid crystals with suitable temperature range. As temperature changes, figures show up in different colours.

(ii) Electrical devices:

Liquid crystals are used in display of electrical devices such as digital watches, calculators and Laptop computers. These devices operate due to fact that temperature, pressure and electro-magnetic fields easily affect weak bonds, which hold molecules together in liquid crystals.

(iii) Chromatography:

In chromatographic separations, liquid crystals are used as solvents.

(iv) Oscillographic:

Oscillographic and TV displays also use liquid crystal screens.

Q.6.(a) Give the four applications of Dalton's law of partial pressure. (4)

Ans Following are the four important applications of Dalton's Law of partial pressure:

1. Some gases are collected over water in the laboratory. The gas during collection gathers water vapours and becomes moist. The pressure exerted by this moist gas is, therefore, the sum of the partial pressures of the dry gas and that of water vapours. The partial pressure exerted by the water vapours is called aqueous tension.

$$P_{moist} = p_{dry} + p_{w.vap}$$
$$P_{moist} = p_{dry} + \text{aqueous tension}$$
$$P_{dry} = p_{moist} - \text{aqueous tension}$$

While solving the numericals, the aqueous tension is subtracted from the total pressure (P_{moist}).

2. Dalton's law finds its applications during the process of respiration. The process of respiration depends upon the difference in partial pressures. When animals inhale air then oxygen moves into lungs as the partial pressure of oxygen in the air is 159 torr, while the partial pressure of oxygen in the lungs 116 torr. CO_2 produced during respiration moves out in the opposite direction, as it's partial pressure is more in the lungs than that in air.

3. At higher altitudes, the pilots feel uncomfortable breathing because the partial pressure of oxygen in the un-pressurized cabin is low, as compared to 159 torr, where one feels comfortable breathing.

4. Deep sea divers take oxygen mixed with an inert gas say He and adjust the partial pressure of oxygen according to the requirement. Actually, in sea after every 100 diver experiences approximately 3 atm pressure, so normal air cannot be breathed in depth of sea. Moreover, the pressure of N_2 increases in depth of sea and it diffuses in the blood.

(b) How charge on electron is measured by using Millikan's oil drop method? (4)

Ans In 1909, Millikan determined the charge on electron by a simple arrangement. The apparatus consists of a metallic chamber. It has two parts. The chamber is filled with air, the pressure of which can be adjusted by a vacuum pump. There are two electrodes A and A'. These are used to generate an electric field in the space between the electrodes. The upper electrode has a hole.

A fine spray of oil droplets is created by an atomizer. A few droplets pass through the hole in top plate and into the region between the charged plates, where one of them is observed through a microscope. This droplet appears in the microscope as a bright speck against a dark background. The droplet falls under the force of gravity without applying the electric field. The velocity of the droplet is determined. The velocity of the droplet (v_1) depends upon its weight, mg

$$V_1 \propto mg \qquad (1)$$

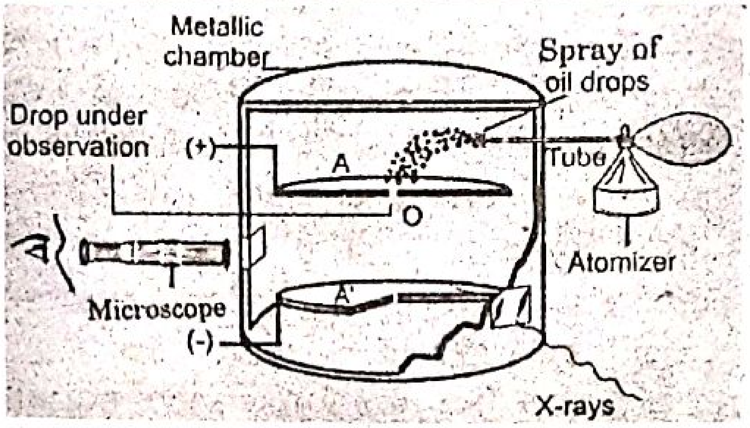

Fig. Millikan's oil drop method for determine of charge of electron.

where 'm' is the mass of the droplet and 'g' is the acceleration due to gravity. After that the air between the electrodes is ionized by x-rays. The droplet under observation takes up an electron and gets charged. Now connect A and A' to a battery which generates an electric field having a strength, E. The droplet moves upwards against the action of gravity with a velocity (V_2).

$$V_2 \propto E_e - mg \qquad (2)$$

where 'e' is the charge on electron and E_e is the upward driving force on the droplet due to applied electric field strength E.

Dividing equation (1) by (2),

$$\frac{V_1}{V_2} = \frac{mg}{E_e - mg} \qquad (3)$$

The values of V_1 and V_2 are recorded with the help of microscope. The factors like g and E are also known. Mass of the droplet can be determined by varying the electric field in such a way that the droplet is suspended in the chamber. Hence, 'e' can be calculated.

By changing the strength of electric field, Millikan found that charge on each droplet was different. The smallest charge which he found was 1.59×10^{-19} coulombs, which is very close to the recent value of 1.6022×10^{-19} coulombs. This smallest charge on any droplet is the charge of one electron. The other drops having more than one electron on them have double or triple the amount of this charge. The charge present on an electron is the smallest charge of electricity that has been measured so far.

Q.7.(a) Define enthalpy and prove that $q_p = \Delta H$. **(4)**

Ans **Enthalpy:**

A quantity of heat q is given to the system (gas) which is now kept at constant atmospheric pressure. A part of this heat is used to increase the internal energy of the gas and the rest is used to do work on the surroundings. This work is done by the gas, when it expands against a constant pressure. To take account of increase in internal energy and accompanying work done by the gas, there is another property of the system called enthalpy or heat content. It is represented by H. In general, enthalpy is equal to the internal energy, E plus the product of pressure and volume (PV).

$$H = E + PV$$

Enthalpy is a state function. It is measured in joules. It is not possible, to measure the enthalpy of a system in a given state. However, change in enthalpy (ΔH) can be measured for a change in the state of system. A change in enthalpy of a system can be written as:

$$\Delta H = \Delta E + \Delta(PV)$$

or $$\Delta H = \Delta E + V\Delta P + P\Delta V$$

Since, the gas in kept at constant pressure, $\Delta P = 0$

Hence, $$\Delta H = \Delta E + P\Delta V \qquad \text{(i)}$$

In case of liquids and solids, the changes in state do not cause significant volume change *i.e.,* $\Delta V = 0$. For such process, ΔH and ΔE are approximately the same *i.e.,* $\Delta H \approx \Delta E$.

According to first law of thermodynamics,

$$\Delta E = q + w$$

If w is pressure-volume work done by the system, then

$$w = -P\Delta V$$

So, $$\Delta E = q - P\Delta V$$

Putting the value of ΔE in equation (4), we get

$$\Delta H = q - P\Delta V + P\Delta V$$

$$\Delta H = q$$

Since, the pressure is constant, therefore,

$$\Delta H = q_p \qquad \text{(ii)}$$

This shows that change in enthalpy is equal to heat of reaction at constant pressure. The reactions are carried out at

constant pressure more frequently than at constant volume. So, working with ΔH is more convenient rather than ΔE.

(b) Explain paramagnetic nature of O_2 according to molecular orbital theory. (4)

Ans **Oxygen O_2:**

The formation of molecular orbitals in oxygen molecule is shown in Fig.

The electronic configuration O2 is

$\sigma(1s)^2 < \sigma^*(1s)^2 < \sigma(2s)^2 < \sigma^*(2s)^2 < \sigma(2p_x) < \pi(2p_y)^2 = \pi(2p_z)^2 < \pi^*(2p_y)^1 = \pi_z^*(2p_z)^1 < \sigma^*2p_x$

The bond order in O_2 is $\frac{6-2}{2} = 2$, which corresponds to a double bond.

This is consistent with the large bond energy of 496 kJ mol^{-1} of oxygen molecule.

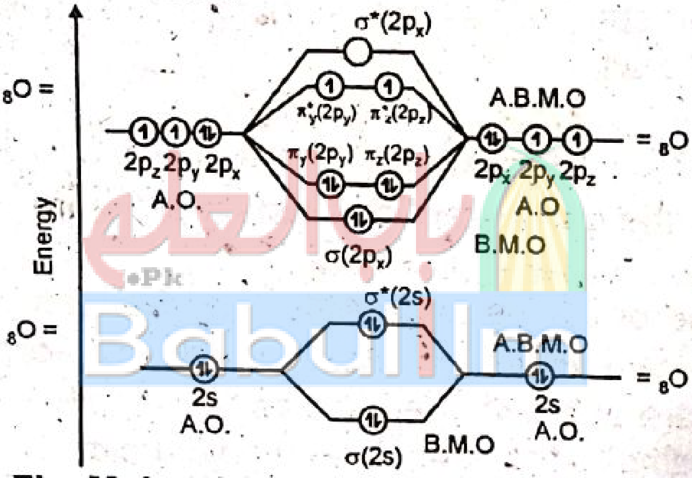

Fig. Molecular orbitals in O_2 molecule.

Fig. shows that the filling of molecular orbitals leaves two unpaired electrons in each of the $\pi^*(2p_y)$ and $\pi^*(2p_z)$ orbitals. Thus, the electronic configuration of the molecular orbitals accounts admirably for the paramagnetic properties of oxygen. This is one of the greatest successes of the molecular orbital theory. Liquid O_2 is attracted towards the magnet.

Anyhow, when two more electrons are given to O_2, it becomes O_2^{2-}. The paramagnetism vanishes. Similarly, in O_2^{2+}, the unpaired electrons are removed and paramagnetic property

is no more there. Bond order of O_2^{2-} and are also different from O_2 and are one and three, respectively.

Similarly, M.O.T justifies that F_2 has bond order of one and Ne does not make a bond with Ne.

Q.8.(a) The solubility of CaF_2 in water at 25°C is found to be 2.05×10^{-4} mol dm^{-3}. What is the value of K_{sp} at this temperature? (4)

Ans CaF_2 is a sparingly soluble salt. In order to know the concentration of the ions:

Reaction:

Let us write down the following equation

$$CaF_2 \rightleftharpoons Ca^{2+} + 2F^{-}$$

Data:

The concentration of Ca^{2+} at equilibrium stage:

$$= 2.05 \times 10^{-4} \text{ mol dm}^{-3}$$

The concentration of F^{-} at equilibrium stage

$$= 2 \times 2.05 \times 10^{-4} \text{ mol. dm}^{-3}$$

$$= 4.1 \times 10^{-4} \text{ mol. dm}^{-3}$$

Solubility product K_{sp} at 25°C

Formula applied:

Formula of solubility product

$$K_{sp} = [Ca^{2+}][F^{-}]^2$$

Putting the values of concentrations

$$K_{sp} = 2.05 \times 10^{-4}(4.1 \times 10^{-4})^2$$

$$K_{sp} = 2.05 \times 10^{-4} \times 16.81 \times 10^{-8}$$

$$K_{sp} = 34.46 \times 10^{-12}$$

$$\boxed{K_{sp} = 3.446 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}}$$

(b) What is order of reaction? Describe two methods for finding order of reaction. (Half-life method and method of large excess) (4)

Ans **Order of Reaction:**

"The order of a reaction is the sum of exponents of the concentration terms in the rate expression of that reaction."

It can be determined by the following methods:

1. Half-life method 2. Method of large excess

Here, we will only discuss half-life method and the method of large excess

1. Half-life method:

Half-life of a reaction is inversely proportional to the initial concentration of reactants raised to the power one less than the order of reaction.

Therefore, $(t_{1/2})_n \propto \frac{1}{a^{n-1}}$

Let us perform a reaction twice by taking two different initial concentrations 'a_1' and 'a_2' and their half-life periods are fond to be t_1 and t_2 respectively.

$$t_1 \propto \frac{1}{a_1^{n-1}} \quad \text{and} \quad t_2 \propto \frac{1}{a_2^{n-1}}$$

Dividing the two relations:

$$\frac{t_1}{t_2} = \left[\frac{a_2}{a_1}\right]^{n-1}$$

Taking log on both sides:

$$\log\frac{t_1}{t_2} = (n-1)\log\left[\frac{a_2}{a_1}\right]$$

Rearranging,

$$n = 1 + \frac{\log\left[\frac{t_1}{t_2}\right]}{\log\left[\frac{a_2}{a_1}\right]}$$

So, if we know the two initial concentrations and two half-life values, we can calculate the order of reaction (n).

$$n = 1 + \frac{0.0802}{0.0940}$$

$$n = 1 + 0.85 = 1.85 \approx 2$$

1.85 is close to 2, hence the reaction is of second order.

2. Method of Large Excess:

In this method, one of the reactants is taken in a very small amount as compared to the rest of the reactants. The active masses of the substances in large excess remain

constant throughout. That substance taken in small amount controls the rate and the order is noted with respect to that.

The reason is that a small change in concentration of a substance taken in very small amount affects the value of rate more appreciably. The hydrolysis of ethyl acetate as mentioned earlier shows that water being in large excess does not determine the order.

In this way, the reaction is repeated by taking rest of the substances in small amounts one by one and overall order is calculated.

Q.9.(a) What is hydration and hydrolysis? Describe with two examples in each. (4)

Ans **Hydration:**

"The crystalline substances which contain chemically combined water in definite proportion is called a hydrate."

Examples:

(i) $CuSO_4$ is pentahydrated. Four water molecules are attached with Cu^{2+} and one with SO_4^{2-}. The reason is that Cu^{2+} has a greater charge density.

(ii) $(COOH)_2.2H_2O$

Hydrolysis:

"The reaction of the anion or cation of a salt with water to produce a slightly basic or acidic solution is called hydrolysis."

The hydrolysis of the salts mentioned are shown as follows:

$$NH_4Cl + H_2O \rightleftharpoons NH_4OH + H^+ + Cl^-$$

$$AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3H^+ + 3Cl^-$$

(b) Write a note on standard hydrogen electrode. How is it used to determine the electrode potential? (4)

Ans **SHE:**

A standard hydrogen electrode is used as a standard. It consists of a piece of platinum foil, which is coated with finally divided platinum black to give it a large surface area and suspended in one molar solution of HCl. The potential of this electrode is arbitrarily taken as zero.

Measurement of Electrode Potential:

In any measurement of electrode potential, the concerned electrode is joined electrolytically with SHE and galvanic cell is established.

To measure the electrode potential of zinc, a galvanic cell is established between zinc electrode dipped in 1 M solution of its ions and SHE at 25°C. Under standard conditions, the voltmeter reads 0.76 volts and the deflection is in such a direction as to indicate that zinc has greater tendency to give off electrons than hydrogen ions. In other words, the half reaction of zinc has greater tendency to occur than reaction of hydrogen.

$$Zn_{(s)} \longrightarrow Zn^{+2} + 2e^- \quad \text{(greater tendency)}$$

$$H_{2(g)} \longrightarrow 2H^+ + 2e^- \quad \text{(slower tendency)}$$

The voltage is 0.76 volts. The standard electrode potential of zinc is, therefore, 0.76 volts. It is called oxidation potential of Zn and is given the positive sign. The reduction potential of Zn-electrode is −0.76 volts. The electrode reactions will be shown as follow:

At anode:

$$Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2e^- \quad \text{(oxidation)}$$

At cathode:

$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)} \quad \text{(reduction)}$$

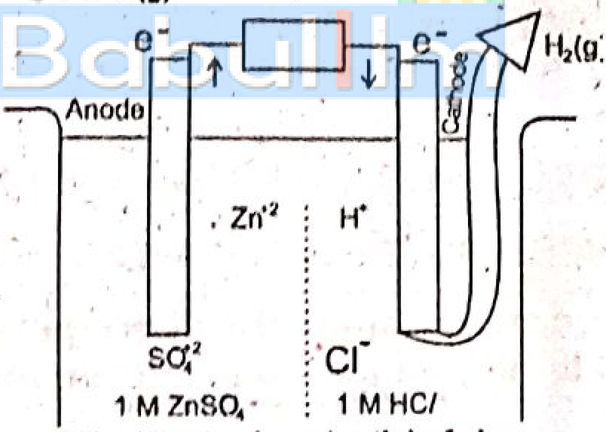

Fig. Electrode potential of zinc.